

**REMARKS**

The Office Action mailed November 20, 2008 has been carefully considered and the following response prepared. Claims 1-16 are pending in the application.

**REJECTION UNDER 35 USC 112, FIRST PARAGRAPH**

At page 2 of the Office Action, the Examiner rejected claims 1-16 under 35 USC 112, first paragraph as not enabled. The Examiner stated the instant claims employ sulfosuccinates and sulfonamide herbicides broadly, whereas the declaration provides unexpected results related to stability and particle size for compositions specifically comprising foramsulfuron or iodosulfuron as the sulfonamide herbicide plus Triton GT-7ME as the sulfosuccinate. The Examiner alleged that it would require undue experimentation to determine stability and particle size data for claimed compositions not containing foramsulfuron or iodosulfuron as the sulfonamide herbicide, plus Triton GT-&ME as the sulfosuccinate plus rheological additives and dispersants/emulsifiers in order to support the broad limitation to sulfonamide herbicide and sulfosuccinate in the instant claims.

Applicants traverse this rejection.

The Examiner contended that undue experimentation would be required to determine stability and particle size data for claimed compositions not containing foramsulfuron or iodosulfuron as the sulfonamide herbicide, plus Triton GT-&ME as the sulfosuccinate plus rheological additives and dispersants/emulsifiers in order to support the broad limitation to sulfonamide herbicide and sulfosuccinate in the instant claims. Applicants strongly disagree. There has never been a requirement that every species encompassed by a claim must be disclosed or exemplified in a working example. *In re Angstadt*, 537 F.2d 498 (CCPA 1976). In order to meet the enablement requirement, not all formulations within the scope of the claims need to be exemplified, nor does stability and particle size data need to be provided. Rather the standard for enablement is “to teach those of ordinary skill how to make and use the invention as broadly as it is claimed.” *In re Vaeck*, 947 F.2d 488, 496 & n. 23 (Fed. Cir. 1991), quoted in *Enzo Biochem, Inc. v. Calgene, Inc.*, 188 F.3d 1362, 1374 (Fed. Cir. 1999). There must be

sufficient disclosure, either through illustrative examples or terminology, to teach those of ordinary skill how to make and use the invention as broadly as it is claimed. Some experimentation, even a considerable amount, is not “undue” if, e.g., it is merely routine, or if the specification provides a reasonable amount of guidance as to the direction in which the experimentation should proceed. See *In re Wands*, 858 F.2d 731, 737 (Fed. Cir. 1988).

Applicants have provided sufficient description and illustrative examples in the specification and the declaration of Dr. Deckwer<sup>1</sup> to enable persons skilled in the art to make and use the invention as claimed without undue experimentation. The Examiner’s conclusion that undue experimentation would be required for persons skilled in the art to determine stability or particle size for claimed compositions containing sulfonamides other than foramsulfuron or iodosulfuron is not understood. These two sulfonylurea compounds were selected as exemplary compounds to demonstrate the stability and particle size in the claimed oil suspension concentrates in more detail. The specification states at page 93, lines 20-27 that the oil suspension concentrates of the invention have excellent chemical and physical stability. The ability of various types of sulfonamide herbicides, including sulfonylaminocarbozyltriazolinones and sulfonylureas, to be formulated according to the present invention can be clearly seen from the declaration of Dr. Deckwer in Examples 3 and 4 and Table 3. Table 3 shows that formulations of the invention, wherein the sulfonamide is foramsulfuron, mesosulfuron, ethoxysulfuron, propoxysulfuron, flucarbazone, compound A21.1<sup>2</sup>, or thifensulfuron, all show good chemical stability and physical stability during storage for eight weeks at 40°C. The teachings of the specification clearly provide a solution for stability /particle size problems that can occur with the new oil suspension concentrate type of formulation. This is clearly accomplished by providing detailed data for two sulfonamide herbicides and additional data for several other sulfonamide herbicides.

The disclosure of the specification and examples provide ample guidance for preparing and using the claimed oil suspension concentrates. Sulfonamides are disclosed at pages 3-17 of

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<sup>1</sup> The declaration of Dr. Deckwer was submitted with Applicants’ response filed July 3, 2008.

<sup>2</sup> Structure as disclosed in the specification; now known under the common name thiencarbazone, as shown in the attached Exhibit A, the entry for the compound in the Compendium of Pesticide Common Names)

the specification. Safeners are disclosed at pages 17-21 of the specification. Organic solvents are disclosed at pages 31-35 of the specification. Sulfosuccinates are disclosed at pages 35-39 of the specification. Methods of preparing the oil suspension concentrates are disclosed in the speciation at pages 88-89, 93-94 and the examples. The physical and/or chemical stability of the claimed oil suspension concentrates can be determined using routine tests known in the art, such as the storage tests used in the examples and the declaration of Dr. Deckwer.

The specification thus enables the oil suspension concentrates of claims 1-16. Withdrawal of this section 112, first paragraph rejection is respectfully requested.

### **REJECTION UNDER 35 USC 103**

At page 7 of the Office Action the Examiner maintained the rejection of claims 1-16 under 35 USC 103 as being unpatentable over the combined teachings of Schnabel et al. (U.S. Patent 6,693,063), Wurtz et al. (U.S. Published application 2002/0016263) and Sixl (U.S. Patent 6,479,432). The Examiner alleged that it would have been *prima facie* obvious to the ordinary artisan at the time the invention was made to have combined Applicants' components in a single herbicidal oil suspension concentrate because the prior art teaches that it was well known in the art to combine the disclosed sulfonylurea herbicides, safeners, and solvents in a suspension concentrate, and because Wurtz et al specifically discloses the utility of adding the sulfosuccinate esters in these compositions. The Examiner further alleged that all of the cited references are in the herbicide art and therefore it would have been expected that their combination would yield a composition that successfully functions as an herbicide.

Applicants again traverse this rejection. Applicants' remarks relating to this rejection in the response filed July 3, 2008 are incorporated by reference in the present response.

Claim 1 is directed to an oil suspension concentrate, comprising a) one or more herbicidally active compounds from the group of the sulfonamides in suspended form, b) one or more safeners, c) one or more organic solvents, and d) one or more sulfosuccinates. Claims 2-16 depend directly or indirectly from claim 1.

Schnabel et al., Wurtz et al. and Sixl are each concerned with herbicidal compositions. However, the mere fact that references can be combined or modified does not render the resultant combination obvious unless the results would be been predictable to one of ordinary skill in the art. *KSR International Co. v. Teleflex Inc.* 127 S. Ct 1727, 82 USPQ 2d 1385, 1396 (2007). As discussed in Applicants' previous response, formation of crystals by the active compound in liquid suspension concentrates was an art-recognized problem, as shown in the description of oil based suspension concentrates submitted as Exhibit B with Applicants' response filed July 3, 2008. Solutions for the problems of physical stability of the newly developed oil suspension concentrates could not be obtained by the combination of the teaching for a suspension concentrate formulation (Sixl) with the teachings for emulsion concentrate formulations (Schnabel et al. and Wurtz et al.). Schnabel et al., Sixl and Wurtz et al. are silent on the need to reduce the formation of crystals consisting of the active compound, which ultimately would lead to the undesired formation of plaques. A person skilled in the art would not have been aware of this potential problem that could surface from the reading of any of the cited references, much less be led to the formation of the present invention in the expectation that the detrimental formation of crystals could be suppressed. Applicants therefore again respectfully disagree with the Examiner's assertion that one can arrive at the formulation of the present invention from the combination of the teachings of Schnabel et al., Sixl and Wurtz et al. since the problem of crystal formation was not identified in any of the cited references.

Typically, a dispersion of solid particles in a liquid is thermodynamically unstable. This means that the dispersion tends to reduce its solid-liquid surface area, to reduce its free solid-liquid surface energy, to achieve a thermodynamically stable state. The average size of particles in a dispersion grow ("particle growth"), and the dispersion becomes instable and forms sediments. This technical aspect of particle growth is called the "Ostwald ripening", which leads to a destabilization of a dispersion of particles in a liquid. (see The Colloidal Domain, D.F. Evans, H. Wennerström, 2<sup>nd</sup> Ed., 1999 Wiley-VCH, pages 66-67, Chapter 2.3.2, and Colloidal Dispersions, I.D. Morrison, S. Ross, 2002, J.Wiley and Sons, pages 151-152, Chapter 6.6, submitted herewith as Exhibits B and C, respectively.

The rate of particle growth is mainly driven by the solubility of the dispersed compound in the liquid (see Colloidal Dispersions, I.D. Morrison, S. Ross, 2002, J. Wiley and Sons, page 444, Chapter 22.12.c, and Growth and Coarsening, L. Ratke, P.W. Voorhees, 2002, Springer, pages 117-126, Chapter 6, submitted herewith as Exhibits D and E, respectively. When the solubility of the particles in a dispersion is zero, no Ostwald ripening occurs. However, when the particles in a dispersion are partly soluble, Ostwald ripening occurs, because increasing solubilities cause increasing/higher growth rates regarding the unwanted particle growth.

Wurtz et al. describes the effect of chemical stabilization and solubilization of an active ingredient in an organic liquid by special surfactants, namely sulfosuccinates, to form an emulsion concentrate. In the case of a dispersion of solid particles in an oil suspension concentrate, this increase in solubility should lead to an increasing/higher rate of particle growth and to an accelerated formation of sediment (collapsing of the dispersed system). This is not the case for sulfosuccinates and the active ingredients, which are dispersed in an organic liquid, according to the present invention, because the claimed oil suspension concentrates show no Ostwald ripening, and are therefore stable against sedimentation. The claimed oil suspension concentrates thus operate in a manner contrary to the aforementioned established scientific concepts. These results would not be predictable to one of ordinary skill in the art. The oil suspension concentrates of the present invention could not be obtained simply from the reading of Schnabel et al., Sixl and Wurtz et al. It is apparent that the claimed oil suspension concentrates are neither disclosed nor suggested by the combination of Schnabel et al., Sixl and Wurtz et al. and are not obvious in view of the cited references.

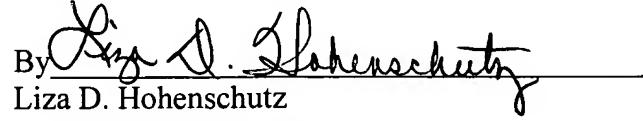
In summary, Applicants submit that a *prima facie* case of obviousness has not been established with regard to claims 1-16. Withdrawal of this section 103 rejection is again respectfully requested.

In view of the above the present application is believed to be in a condition ready for allowance. Reconsideration of the application is respectfully requested, and an early Notice of Allowance is earnestly solicited.

The Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Deposit Account No. 03-2775, under Order No. 09879-00039-US.

Dated: April 20, 2009

Respectfully submitted,

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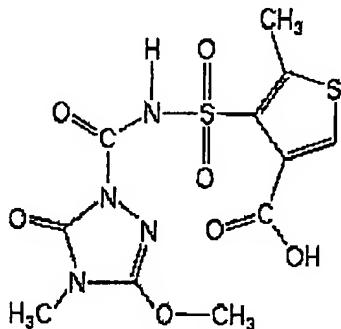
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**EXHIBIT A**

# thiencarbazone

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STATUS: ISO 1750 (published)  
IUPAC: 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl) carbonylsulfamoyl]-5-methylthiophene-3-carboxylic acid  
CAS: 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl) carbonylamino]sulfonyl]-5-methyl-3-thiophenecarboxylic acid  
REG. NO.:  
FORMULA: C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>O<sub>7</sub>S<sub>2</sub>  
ACTIVITY: herbicides (triazolone herbicides)  
NOTES: When this substance is used as an ester or a salt, its identity should be stated, for example thiencarbazone-methyl [317815-83-1].  
STRUCTURE:



PRONUNCIATION: thi-ěn-karb-a-zōn [Guide to British pronunciation](#)

INCHI: InChI=1/C11H12N4O7S2/c1-5-7(6(4-23-5)8(16)17)24(20,21)13-9(18)15-11(19)14(2)10(12-15)22-3/h4H,1-3H3,(H,13,18)(H,16,17)/f/h13,16H

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A data sheet from the Compendium of Pesticide Common Names

**EXHIBIT B**

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# THE COLLOIDAL DOMAIN

## Where Physics, Chemistry, Biology, and Technology Meet

Second Edition

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and  
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WILEY-VCH

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Solution:

(a) When  $\theta < 10^\circ$  we have  $\cos \theta \approx 1$ .

$$\ln(p_0/p) = \frac{2(18 \times 10^{-6} \text{ m}^3)(72 \times 10^{-3} \text{ J/m}^2)}{(1 \times 10^{-6} \text{ m})(2.5 \times 10^3 \text{ J})} = 0.1$$

$p = 0.91p_0$  or 91% relative humidity.

(b) When  $q = 115$ ,  $\cos \theta = -0.42$ , and  $p = 1.04p_0$  and water will only condense in the gap when the air is 4% supersaturated with water vapor.

An interesting aspect of eq. 2.3.6 is that for  $\theta > 90^\circ$  (so that  $\cos \theta < 0$ ), the vapor will be less likely to condense in the gap than in the bulk. This tendency implies that if we consider the reverse process of a liquid filling the system that approaches the boiling point, the vapor is preferentially formed in the gap. Because the vapor has a much lower density, the contribution from the surface free energy is much larger, counted per molecule in the gap. Vaporization typically occurs at larger critical separation for  $\cos \theta < 0$  than for the condensation when  $\cos \theta > 0$ .

An actual solid surface is normally rough. It may contain cracks, and pores can lead to the interior of the solid. For such a surface in equilibrium with a vapor, the more macroscopic phenomena of a condensation of a nonwetting liquid may occur in addition to physical and chemical adsorption. The final result of the condensation events depends on general thermodynamic properties, such as vapor pressure, contact angle, and surface tension, as well as on the local geometry of the surface. Clearly, the finer the cracks or pores, or the rougher the surface, the more the liquid is likely to condense.

### 2.3.2 Surface Free Energies Govern the Growth of Colloidal Particles

Consider a dispersion of colloidal particles that have been formed by precipitating a new phase from solution. The "particles" may be either solid or liquid; they may even take the form of gas bubbles. Their constituent molecules are present as a solute in the liquid at a saturation concentration. Molecules exchange between the particles and the solution so that each particle is in local equilibrium with the solution close to it.

The free energy of a particle  $i$  with  $n_i$  molecules and area  $A_i$  consists of a bulk term,  $n_i \mu_p^b$ , plus a surface term  $A_i \gamma_{ss}$ , where  $\gamma_{ss}$  stands for the particle-solution surface free energy. The free energy change  $\Delta G_i$  caused by taking a molecule from the solution at concentration  $c$ , and adding it to particle  $i$ , is

$$\Delta G_i = (\mu_p^b - \mu_p^s) - kT \ln c_i + \gamma_{ss} \Delta A_i \quad (2.3.7)$$

This free energy change equals zero at local equilibrium.

The area change,  $\Delta A_i$ , upon adding a molecule to the particle depends on the size of the particle. For spherical particles of radius  $R_i$ , the volume is

$$\frac{4\pi}{3} R_i^3 = n_i V_M \quad (2.3.8)$$

where  $V_M$  represents the volume per molecule. Thus, increasing  $n_i$  by one leads to a change in the radius by

$$\Delta R_i = \frac{V_M}{A_i} \quad (2.3.9)$$

and the corresponding area change is

$$\Delta A_i = \frac{2V_M}{R_i} \quad (2.3.10)$$

This equation shows that the larger the particle, the smaller will be the area change and the smaller the surface energy term in eq. 2.3.7. At local equilibrium,  $c_i$  becomes smaller as the particle becomes larger.

In a dispersion containing both large and small particles, the solute concentration is higher close to the small ones, and a diffusional flow of solute moves from the small particles to the large ones. As a result, the small particles decrease in size and dissolve and the large ones grow. This process is called Ostwald ripening. As we will discuss later, Ostwald ripening provides one important mechanism for destabilizing colloidal dispersions.

### 2.3.3 Surface Free Energies Oppose the Nucleation of a New Phase

It is a common observation that liquids can be heated somewhat above the equilibrium boiling point before vapor bubbles actually form. Similarly, a vapor can be brought to a temperature/pressure below the boiling point before liquid drops actually appear in the bulk phase, and a liquid can remain intact even when cooled to below the freezing point. The time stability of metastable states depends on the kinetics of the different processes leading to the formation of the stable new phase. We say that the new phase must nucleate and that the surface free energy of the new interface makes nucleation a sluggish process.

For example, let us consider the nucleation of a liquid phase from a vapor of pressure  $p$ . The free energy change of forming a liquid drop of radius  $R$  is

$$\begin{aligned} \Delta G &= -nkT \ln\left(\frac{p}{p_0}\right) + 4\pi R^2 \gamma \\ &= -\frac{4}{3}\pi \frac{R^3}{V_M} kT \ln\left(\frac{p}{p_0}\right) + 4\pi R^2 \gamma \quad (2.3.11) \end{aligned}$$

**Exhibit C**

# **COLLOIDAL DISPERSIONS**

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**SUSPENSIONS, EMULSIONS,  
AND FOAMS**

Ian D. Morrison  
Sydney Ross



A John Wiley & Sons, Inc., Publication

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are more soluble than the larger ones so that the spontaneous process is for molecules in small droplets to transfer to larger droplets. The large droplets spontaneously grow at the expense of the smaller droplets, another instance of Ostwald ripening.

Many natural and manufactured products are emulsions, for example, foods, cosmetics, pharmaceuticals, paints, petrochemicals, explosives, and agrochemicals. The gradual increase in the droplet size and size distribution can be monitored *in situ* by ultrasonic attenuation and compared to theories for Ostwald ripening.<sup>17</sup>

The rate of Ostwald ripening depends on the transport mechanism for molecules from the small drop to reach the larger ones. The rate at which molecules in the disperse phase can leave surfactant-covered surfaces and the rate at which molecules penetrate the surfactant-covered surfaces of larger drop is significant and may be rate determining. The role of adsorption and desorption of molecules in micelles can also be important.<sup>18</sup>

Although solid particles are not usually spherical, the general conclusion that small particles have a higher solubility than large particles is well established, as is the requirement of supersaturation before nucleation occurs in clean systems, and the phenomenon of the Ostwald ripening (digestion) of precipitates.

The fierce debate about the existence of anomalous water or, as it was popularly known, "polywater," arose when investigators found that water, in capillaries of a few microns radius, had a much lower vapor pressure than predicted by the Kelvin equation. The debate ended with the discovery that the "anomalous" behavior is accounted for by the presence of various leachable impurities in solution.<sup>19</sup>

### 6.7 CAPILLARY OR LAPLACE FLOW

*Capillary flow* of a liquid results from differences of hydrostatic pressure within a liquid, created by local differences of curvature of the liquid surface. The pressure is less on the convex side of an interface; liquid at higher pressure then flows to the region of lower pressure. A liquid that makes a low angle of contact in a narrow vertical tube creates a meniscus that is convex to the liquid; consequently, liquid flows up the tube. Mercury in a glass tube creates a meniscus that is concave to the liquid, consequently, mercury sinks in the tube, but since the density of mercury is large, the decline of the mercury level in the tube is small; nevertheless a correction for this capillary effect has to be introduced in precise mercury manometry. The minimum pressure,  $\Delta p$ , required to prevent the rise of a liquid in a capillary tube of radius  $r$ , is also a result of the curvature of the liquid surface.

$$\Delta p = \frac{2\sigma \cos \theta}{r} \quad (6.46)$$

The more acute the angle of contact, the greater the pressure required to prevent liquid rising; if the angle is  $90^\circ$ , no pressure is required; if the angle is obtuse, the liquid will not enter the tube spontaneously.

sphere and  $p_0$  equal to the vapor pressure of a plane surface, gives

$$\ln \frac{p}{p_0} = \frac{2\sigma V_m}{aRT} \quad (6.43)$$

where  $a$  is the radius of the drop. Equation (6.43) is one form of the Kelvin equation where  $p > p_0$  as in a convex surface. It states that small drops have higher vapor pressure than flat sheets of liquid, hence small drops evaporate more readily. Conversely, the condensation of small drops from the vapor requires so much supersaturation that the process does not occur spontaneously in the absence of solid particles to act as nucleating sites. Once small drops are nucleated, they grow rapidly as their equilibrium pressure declines.

The Kelvin equation, (6.43), also applies to the curved surface of a liquid meniscus. Where  $r$  is the radius of curvature of the meniscus,

$$\ln \frac{p}{p_0} = -\frac{2\sigma V_m}{rRT} \quad (6.44)$$

where  $p < p_0$  as in a concave surface.

Equation (6.44) states that the vapor pressure of a liquid is decreased at a concave meniscus, such as occurs on a wetting liquid in a capillary tube or in the pores of a solid substrate. Experimental verification of the Kelvin equation is reported by Fisher and Israelachvili<sup>15</sup> for the concave meniscus of cyclohexane between crossed cylinders of molecularly smooth mica. With a clean system, where the establishment of equilibrium and the absence of significant contamination could be demonstrated, the Kelvin equation was found to hold for radii of curvature as low as 2.5 nm.<sup>16</sup>

## 6.6 OSTWALD RIPENING

In an aerosol of polydispersed drops in a closed container, the large drops grow at the expense of the smaller ones. The process is known as Ostwald ripening and is common to the coarsening of any finely dispersed phase. It applies to the growth of crystals, the digestion of precipitates and the degradation of emulsions and foams.

Equation (6.43) may be applied to the solubility of small spherical drops in liquids, replacing vapor pressures by saturation concentrations to give the Gibbs-Thomson (or Gibbs-Kelvin) equation

$$\ln \frac{c}{c_0} = \frac{2\sigma V_m}{aRT} \quad (6.45)$$

where  $c$  is the solubility of small spherical droplets of radius  $a$  and  $c_0$  is the solubility of large drops ( $r = \infty$ ). Equation (6.45) implies that the smaller the droplet, the greater its solubility. In a polydisperse emulsion the smaller droplets

**Exhibit D**

# **COLLOIDAL DISPERSIONS**

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**SUSPENSIONS, EMULSIONS,  
AND FOAMS**

**Ian D. Morrison**

**Sydney Ross**



**A John Wiley & Sons, Inc., Publication**

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this occurs, the inverted emulsion has a high concentration and consequently a high viscosity. The usual loss of viscosity on inversion is here a gain of viscosity, but the inverted emulsion has water as the external phase and so can imbibe additional water more readily than before its inversion. The driving force for inversion in such cases is not the close contact of water drops but the massive migration of a predominantly hydrophilic emulsifier out of the oil and into the water.<sup>45</sup>

#### 22.12.b Phase-Inversion Temperature (PIT) Method

Small oil droplets can be formed by emulsifying just below the PIT of the emulsifier. As the temperature is raised toward the PIT, the interfacial tension becomes continuously lower: an example of the Ross-Nishioka effect. When oil is emulsified in water 2–4 degrees below the PIT, the low interfacial tension enables small droplets to form. Once the fine emulsion is made, it is cooled quickly to stabilize it at room temperature.<sup>46</sup> The interfacial tension is now greater but the emulsion has been made.

#### 22.12.c Condensation Methods

Colloidal suspensions of insoluble solids, such as uranic sulfide, barium sulfate, and silver iodide, are made by precipitation reactions in which particle size is limited by promoting a large number of nucleating centers. Fine suspensions are better made by precipitation from solution than by comminution of macroscopic particles. An analogous method to make a fine emulsion is to solubilize an internal phase in micelles. The internal phase may be introduced as a vapor, which nucleates heterogeneously on dust or in micelles, or as a liquid. To obtain small droplets, a large concentration of micelles is required. Since this method depends on a degree of solubility of the internal phase in the medium, in order that molecules may reach the micelles, the same solubility promotes Ostwald ripening, leading to instability. We have already seen how this instability is overcome (see Section 13.3.f) by adding an insoluble coemulsifier to set up a counteracting osmotic pressure within the droplets.

#### 22.12.d Intermittent Milling

An emulsion can be made by shaking two phases together in a test tube. Briggs<sup>47,48</sup> found that emulsification of some systems is much more efficient if the shaking is interrupted by rest periods. For instance, 60% by volume of benzene in 1% aqueous sodium oleate is completely emulsified with only five shakes by hand in about two minutes, if after each shake an interval of 20–25 seconds is allowed. If the shaking is not interrupted, about 3000 shakes in a machine, lasting about seven minutes, is required. Figure 22.14 shows that the time required to make an emulsion with continuous mechanical shaking is much greater than the time required to make the same emulsion with double shakes every 30

**Exhibit E**

ENGINEERING MATERIALS

22 pages

**L. Ratke · P.W. Voorhees**

# Growth and Coarsening

Processing  
in Material Processing



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## 6. Coarsening - Basics and Growth Laws

### 6.1 General considerations on coarsening

Imagine a system consisting of a huge number of particles of a certain phase with different radii embedded in a matrix. Some examples are shown in the introduction in figs. 1.3 and 1.6. Assume further that the alloy is held at a constant annealing temperature. The concentration of solute in the matrix shall be at a level given approximately by the phase diagram and the annealing temperature. What will happen to the dispersion of particles? Generally one will observe in experiments that the particle radii change with annealing time, the average radius will grow, the number of particles decreases, but the overall volume fraction remains nearly a constant. An example of such a behavior is shown in Fig. 6.1. Why do these changes

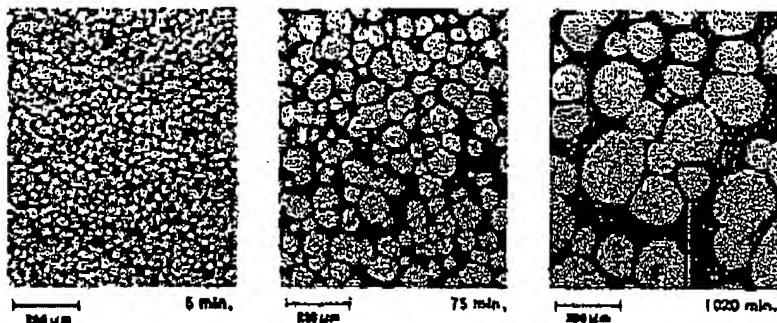


Fig. 6.1. Micrographs of solid tin particles embedded in a eutectic Pb-Sn matrix. The alloy was annealed just above the eutectic temperature for different times as shown in the textlines below the figures.

in particle size occur? Generally speaking, a dispersion of solid or liquid particle in a matrix increases the overall energy due to the existence of interfacial energy associated with the interfacial

area. Since the system tries to minimize the energy, the amount of interfacial area decreases with time. A large number of small particles has, however, more interfacial area than one large particle with the same volume. Thus, the energy contained in the interfacial area of a dispersion increases with the number of particles in the dispersion. Reducing the number of particles decreases the excess energy associated with the interfaces. Therefore, a dispersion coarsens or ripens.

Another important aspect of competitive growth or Ostwald ripening (as explained in more detail in the next section) is its self-similar nature. This *self-similarity*, which occurs after sufficiently long coarsening time, can be understood as the following: take a section through a dispersion (as in figs. 6.1 and 6.2) at two different times and change the magnification by the ratio of the average particle size at these times. Then, the microstructures look similar, see Fig. 6.2. Only the *lengthscale* of the system changes. The *lengthscale* just mentioned is the average particle size, but other *lengthscales* like e.g. the average particle distance or even the inverse of the specific surface area per volume  $1/S_V$  could be used as well. Scaling the radii with the *lengthscale*, one measures the same scaled size distribution. In the following we will set up the growth laws for coarsening. We will use these laws to derive the kinetics and particle size distributions in later chapters.

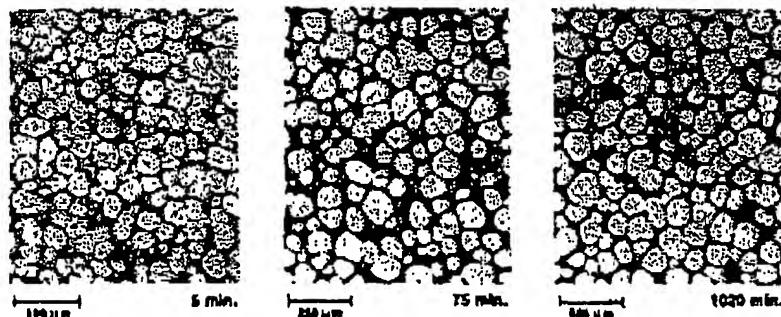


Fig. 6.2. Micrographs of solid tin particles embedded in a eutectic Pb-Sn matrix as already shown in Fig. 6.1 but here we scaled the magnification of each picture by a factor related to the average particle size. All microstructures then look similar.

## 6.2 Ostwald ripening due to curvature supercooling

In the preceding chapters on growth we have discussed the situation of a single sphere growing in a matrix at constant supercooling. Far from the solid particle interface the matrix had a fixed temperature, denoted by  $T_0$  and the interface temperature was given by the equilibrium melting temperature  $T_m$ . We found that the radius of the solid sphere would change proportional to the square root of time. We now examine a different situation. Let us assume that we have a dispersion of spheres with a spectrum of radii embedded in a matrix. The size spectrum is described by a size density distribution  $f(R, t)dR$  (note that  $f dR$  has the units of numbers of particles per volume) at a given time  $t$ . In this case the interface temperature of all particle is no longer equal to the equilibrium melting temperature, but depends on the radius according to the Gibbs-Thomson relation. This has as a consequence that in a closed, adiabatic system the matrix temperature far away from the particle interface is also no longer fixed but determined by a mean field value set by the whole ensemble of spheres. We denote this temperature by  $T_\infty$ . For simplicity we assume here that all solid spheres are so far away from each other that a single sphere approximation can be used with a different boundary condition at infinity, i.e. we assume that the dispersion is very diluted - like the universe is a diluted dispersion of stars. Then, the temperature field looks as depicted in Fig. 6.3. All interfaces of the particles in the dispersion are

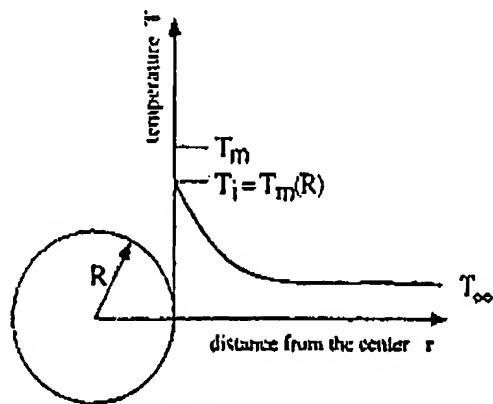


Fig. 6.3. Temperature field around a sphere undergoing radius change due to the combined effect of all other spheres and the Gibbs-Thomson effect.

at a different temperature since the radii are different. This induces locally varying temperature gradients in the matrix. Heat is exchanged within the system between the spheres of different radii. We then have for the growth rate (see eq.(4.40))

$$\frac{dR}{dt} = \frac{\lambda}{\rho L} \frac{T_I(R) - T_\infty}{R}, \quad (6.1)$$

with  $T_I(R)$  as the interface temperature depending on the particle radius according to eq.(2.101)

$$T_I(R) = T_m - \frac{2\Gamma}{R}. \quad (6.2)$$

Inserting this expression into eq.(6.1) leads to

$$\frac{dR}{dt} = \frac{\lambda}{\rho L R} T_m - T_\infty - \frac{2\Gamma}{R}, \quad (6.3)$$

This equation can be brought into simpler form if we introduce artificially the following expression for the far field (mean value) temperature.

$$T_\infty = T_m - \frac{2\Gamma}{R_c}, \quad (6.4)$$

with an as yet unknown radius denoted as  $R_c$ .<sup>1</sup> We will call this radius the critical radius, a notation becoming clearer soon. Let us insert this expression into eq.(6.3). We obtain

$$\frac{dR}{dt} = \frac{2\Gamma\lambda}{\rho L R} \left( \frac{1}{R_c} - \frac{1}{R} \right) \quad (6.5)$$

The meaning of the critical radius becomes clear from this expression. Spheres having that radius have exactly a zero growth rate. The temperature field in a dispersion with many spheres and different radii, and thus interface temperatures according to the Gibbs-Thomson effect, is shown schematically in Fig. 6.4. Assume first that we have the matrix set at a given temperature, let us say the equilibrium melting temperature, and assume that there are no heat losses at the boundary of the matrix, i.e. we isolate it from the environment.

<sup>1</sup> We will show in the next chapter 7 dealing with the statistical analysis of coarsening that the far field temperature is besides a numerical constant equal to the average interface temperature.

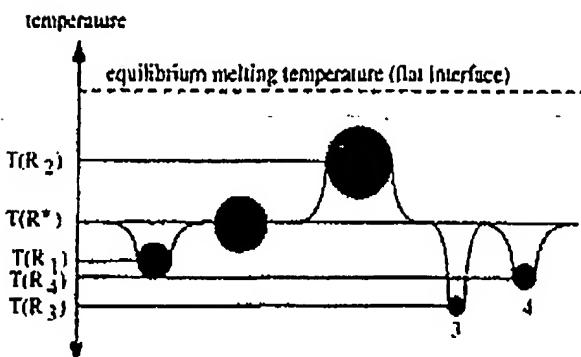


Fig. 6.4. Scheme of the temperature distribution in a dispersion, in which the temperature of the system is defined by the sensible heat exchange between spheres of different melting temperatures according to the Gibbs-Thomson effect.

We then put into the matrix one sphere of radius  $R$ . This sphere has, according to the Gibbs-Thomson relation, a melting temperature slightly lower than the equilibrium melting temperature. Therefore, the sphere will melt thereby consuming, i.e. extracting, heat from the matrix and, thus, if the sphere is sufficiently large lowering the temperature of the matrix until an equilibrium is reached, i.e. the matrix temperature is equal to the radius dependent melting temperature of the sphere. We now proceed and put a huge number of spheres into the matrix. The matrix temperature cannot adjust itself to be in equilibrium with all spheres (and their radius dependent melting temperature) at the same time. Eventually it is able to adjust its temperature to just a value as given in eq.(6.4). A few particles will then be in equilibrium, but others have higher or lower melting temperatures. Thus, the temperature gradients existing in the matrix lead to melting of the smaller spheres and growth of the bigger ones, as shown in Fig. 6.4. Since the smaller ones (smaller than the critical radius) will completely melt, the critical radius has to be redefined (the size distribution changes continuously), leading to a new situation: deciding which particles will now dissolve and which will grow at the expense of the smaller ones. This picture also tells that the problem of ripening cannot be solved without knowledge of the evolution of the size distribution since it defines the critical sphere size. It is also obvious that the mean-field temperature increases continuously towards the equilibrium melting temperature.

As just explained,  $R_c$  is not a constant but changes with time, i.e.  $R_c = R_c(t)$ . Its exact dependence on time will be derived in the following chapters, since it depends on the evolution of the size distribution. Eq.(6.5) can be rearranged to yield

$$\begin{aligned}\frac{dR}{dt} &= \frac{2\lambda\Gamma}{\rho L R} \left( \frac{1}{R_c} - \frac{1}{R} \right) \\ &= \frac{2\lambda\Gamma}{\rho L R^2} \left( \frac{R}{R_c} - 1 \right) = \frac{K_{sl}^*}{R^2} \left( \frac{R}{R_c} - 1 \right),\end{aligned}\quad (6.6)$$

where

$$K_{sl}^* = \frac{2\lambda\Gamma}{\rho L}.\quad (6.7)$$

In contrast to the case with a constant supercooling, this equation cannot be integrated without knowledge of the time dependence of the critical radius.

### 6.3 Ostwald ripening due to solubility changes

The equations governing the coarsening of a two phase mixture consisting of a dispersion of particles in a matrix, in which solute transport governs the change in radius, are quite similar to those for a pure solid-liquid mixture given in the preceding section. The concentration field is sketched in Fig. 6.5. As in the thermally controlled ripening pro-

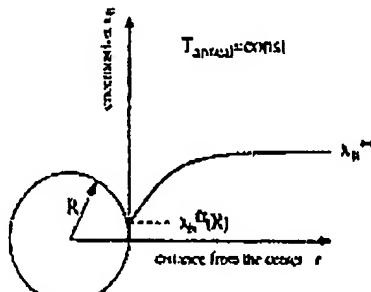


Fig. 6.5. Concentration field around a sphere undergoing radius change due to the combined effect of all other spheres.

cess the concentration at infinity is related to a mean value set by the other particles in the system. We assume again that the whole system

is closed: Mass or species are only exchanged within the system, i.e. between the spheres of different radii. Fig. 6.6 shows how the system establishes a mean field concentration if particles are present with different equilibrium solubilities. The growth rate can be written as (see eq.(4.47))

$$\frac{dR}{dt} = \frac{D}{R} \frac{x_B^\infty - x_B^l(R)}{x_B^g - x_B^a}. \quad (6.8)$$

In principle, the difference  $x_B^g - x_B^a$  depends on the radius. Generally, however, the radius dependence of this difference is small compared to the magnitude of the difference itself and thus can be neglected. We again introduce a critical radius  $R_c$  via

$$x_B^\infty = x_B^{0,c} \left(1 + \frac{f^0}{R_c}\right). \quad (6.9)$$

Inserting this expression into the growth rate eq.(6.8) and using eq.(2.12.1) to express  $x_B^l(R)$  leads to

$$\frac{dR}{dt} = \frac{Df^0}{(x_B^g - x_B^a)R} \left( \frac{1}{R_c} - \frac{1}{R} \right) = \frac{K_{ss}^*}{R^2} \left( \frac{R}{R_c} - 1 \right), \quad (6.10)$$

where

$$K_{ss}^* = \frac{Df^0}{x_B^g - x_B^a}. \quad (6.11)$$

Again we find: In contrast to the situation of constant supersaturation, this equation cannot be integrated without knowledge of the time dependence of the critical radius. Looking at the eqs.(6.6,6.10) we notice that both have the same functional dependence on the radius and the critical radius. The general form for diffusional transport of matter or heat is therefore

$$\frac{dR}{dt} = \frac{K_{diff.}^*}{R^2} \left( \frac{R}{R_c} - 1 \right). \quad (6.12)$$

The difference lies only in the physical meaning of the rate constant,  $K_{diff.}^* = K_{sl}^*$  for ripening in a pure solid-liquid system and  $K_{diff.}^* = K_{ss}^*$  for ripening in an isothermal two-phase alloy.

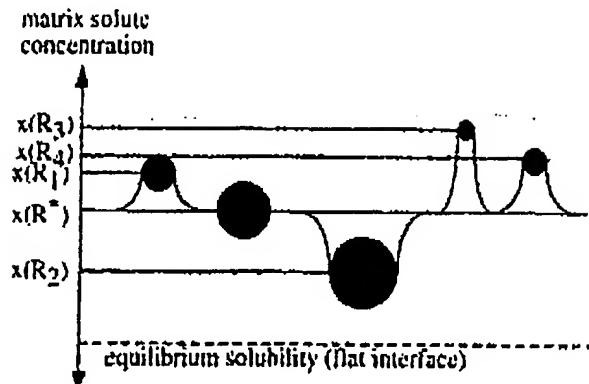


Fig. 6.6. Scheme of the concentration field in a dispersion at constant temperature. The only source of supersaturation shall be the excess solubility of the spheres due to the Gibbs-Thomson effect.

#### 6.4 Ostwald ripening in interface kinetics or general first order reactions

The growth laws derived for interface kinetics of first order for a sphere growing due to concentration and temperature differences were (see eqs.(1.66,1.71))

$$\frac{dR}{dt} = k_s (x_B^0 - x_B^I) \quad (6.13)$$

and

$$\frac{dR}{dt} = k_T (T_I - T_0) \quad (6.14)$$

respectively. Identifying  $x_B^0$  with the far field concentration, eq.(6.9), and  $T_0$  with the far field temperature, eq.(6.4), and using for the interface concentration respectively temperature eqs.(2.124,2.100), we obtain

$$\frac{dR}{dt} = k_s \ell^n \left( \frac{1}{R_c} - \frac{1}{R} \right) \quad (6.15)$$

and

$$\frac{dR}{dt} = 2k_T \Gamma \left( \frac{1}{R_c} - \frac{1}{R} \right). \quad (6.16)$$

In both cases the equation has the general form

$$\frac{dR}{dt} = K_{int.} \frac{1}{R} \left( \frac{R}{R_c} - 1 \right). \quad (6.17)$$

The difference lies only in the physical meaning of the rate constant  $K_{int.}$

$$K_{int.} = \begin{cases} k_s \ell^\alpha & \text{isothermal two-phase alloy} \\ 2k_T \Gamma & \text{pure solid-liquid mixture} \end{cases} \quad (6.18)$$

## 6.5 Coarsening due to a second-order reaction

Now let's assume that the dissolution or growth of a particle is completely controlled by a second-order interface reaction without further qualifying the special microscopic nature of this reaction. In chapter 4 we derived the following relations for the growth rate at constant supersaturation or supercooling:

$$\frac{dR}{dt} = k_s^{2nd} |x_B^0 - x_B'| (x_B^0 - x_B') \quad (6.19)$$

$$\frac{dR}{dt} = k_T^{2nd} |T_m - T_l| (T_m - T_l) \quad (6.20)$$

with the nomenclature described there. Identifying again  $x_B^0$  with the far field concentration eq.(6.9) and  $T_m$  with the far field temperature, eq.(6.4), and using for the interface concentration respectively temperature the eqs.(2.124,2.101), we obtain

$$\frac{dR}{dt} = \frac{k_s^{2nd} (\ell^\alpha)^2}{x_B^{\ell^\alpha, c} - x_B^{0, c}} \frac{1}{R^2} (\rho - 1)^2 \operatorname{sgn}(\rho - 1) \quad (6.21)$$

and thus

$$\frac{dR}{dt} = \frac{K_s^{2nd}}{R^2} (\rho - 1)^2 \operatorname{sgn}(\rho - 1) \quad (6.22)$$

with

$$K_s^{2nd} = \frac{k_s^{2nd} (\ell^\alpha)^2}{x_B^{\ell^\alpha, c} - x_B^{0, c}} \quad (6.23)$$

and  $\rho = R/R_c$ . This was simplified using the relations  $x_B' \sim x_B^0(R) = \ell^\alpha (1/R_c - 1/R) = \ell^\alpha R(\rho - 1)$ . The sgn-function switches the sign when both concentrations are equal, this occurs when  $\rho = 1$ , and thus  $\operatorname{sgn}(x_B' - x_B^0(R)) = \operatorname{sgn}(\rho - 1)$ . For growth in an undercooled melt we obtain

$$\frac{dR}{dt} = 2k_T^{2nd} \Gamma \left( \frac{1}{R_c} - \frac{1}{R} \right) 2\Gamma \left| \frac{1}{R_c} - \frac{1}{R} \right| \quad (6.24)$$

or

$$\frac{dR}{dt} = \frac{K_T^{2nd} 1}{R^2} (\rho - 1)^2 \operatorname{sgn}(\rho - 1) \quad (6.25)$$

with

$$K_T^{2nd} = 2k_T^{2nd} \Gamma^2. \quad (6.26)$$

## 6.6 Coarsening under convective transport

In section 4.6 we derived growth laws of the following kind for cases in which convection outside a diffusion boundary layer dominates mass or heat transport. The growth laws had the general form

$$\frac{dR}{dt} \propto \Delta(x_B, T) \quad (6.27)$$

for Stokes motion of solid particles or Marangoni motion of droplets and

$$\frac{dR}{dt} \propto \Delta(x_B, T) R^{1/2} \quad (6.28)$$

for Stokes motion of droplets. In these equations  $\Delta(x_B, T)$  denotes the difference in concentration or temperature between the particle interface and the far field values, i.e. for supersaturation it means  $\Delta(x_B) = (x_B^\infty - x_B^0)/(x_B^0 - x_B^0)$ . Using the same procedures as before, i.e. identifying  $x_B^\infty$  with the far field concentration in the matrix and using the Gibbs-Thomson relation for  $x_B^0$  we obtain relations of the form

$$\frac{dR}{dt} = \frac{K_1}{R} \left( \frac{R}{R_c} - 1 \right), \quad (6.29)$$

$$\frac{dR}{dt} = \frac{K_2}{R^{1/2}} \left( \frac{R}{R_c} - 1 \right). \quad (6.30)$$

Here the constants  $K_1, K_2$  contain all the physics of the problem. Looking at both equations from a mathematical point of view we see that the first equation, valid for solid particles moving with Stokes velocity or liquid particles moving with Marangoni velocity, is formally identical to that for a first order reaction. Only the physical meaning of the rate constants in all three cases is different. Eq.(6.30), however, gives a new coarsening law and has to be treated separately. We will specify the rate constants after we have solved the complete coarsening problem (see chapter 7).